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TITLE OF THE INVENTION (500 characters max)					
METHODS FOR FABRICATING ISOLATED MICRO-AND NANO-STRUCTURES USING SOFT OR IMPRINT LITHOGRAPHY					
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[Page 1 of 2]

Respectfully submitted,

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June 25, 2004

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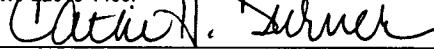
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Cathi H. Turner

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Re: U.S. Provisional Patent Application for METHODS FOR FABRICATING
ISOLATED MICRO- AND NANO-STRUCTURES USING SOFT OR IMPRINT
LITHOGRAPHY
Our Ref. No. 421/110 PROV

Sir:

Please find enclosed the following:

1. Provisional Application Cover Sheet (2 pages) in duplicate;
2. U.S. Provisional Patent Application (49 pages);
3. Seven (7) sheets of drawings;
4. A return-receipt postcard to be returned to our offices with the U.S. Patent and Trademark Office date stamp thereon; and
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UNITED STATES PROVISIONAL PATENT APPLICATION

METHODS FOR FABRICATING ISOLATED MICRO- AND NANO-
STRUCTURES USING SOFT OR IMPRINT LITHOGRAPHY

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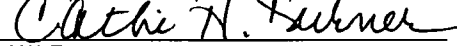
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Cathi H. Turner

DESCRIPTION

METHODS FOR FABRICATING ISOLATED MICRO- AND NANO- STRUCTURES USING SOFT OR IMPRINT LITHOGRAPHY

5

TECHNICAL FIELD

Methods for preparing a patterned structure and methods for forming a pattern on a substrate using soft or imprint lithography. More particularly, methods for preparing a patterned micro or nano-structure and methods for forming a micro- or nano-scale pattern on a substrate using soft or imprint lithography.

10

ABBREVIATIONS

	°C	=	degrees Celsius
15	cm	=	centimeter
	DBTDA	=	dibutyltin diacetate
	DMA	=	dimethylacrylate
	DMPA	=	2,2-dimethoxy-2-phenylacetophenone
	EIM	=	2-isocyanatoethyl methacrylate
20	FEP	=	fluorinated ethylene propylene
	Freon 113	=	1,1,2-trichlorotrifluoroethane
	g	=	grams
	h	=	hours
	Hz	=	hertz
25	IL	=	imprint lithography
	kg	=	kilograms
	kHz	=	kilohertz
	kPa	=	kilopascal
	MCP	=	microcontact printing
30	MHz	=	megahertz

	mL	=	milliliters
	mm	=	millimeters
	mmol	=	millimoles
	mN	=	milli-Newton
5	m.p.	=	melting point
	mW	=	milliwatts
	NCM	=	nano-contact molding
	NIL	=	nanoimprint lithography
	nm	=	nanometers
10	PDMS	=	polydimethylsiloxane
	PFPE	=	perfluoropolyether
	PP	=	polypropylene
	psi	=	pounds per square inch
	PVDF	=	poly(vinylidene fluoride)
15	PTFE	=	polytetrafluoroethylene
	SAMIM	=	solvent-assisted micro-molding
	SEM	=	scanning electron micrograph
	S-FIL	=	"step and flash" imprint lithography
	Si	=	silicon
20	TMPTA	=	trimethylopropane
	μm	=	micrometers
	UV	=	ultraviolet
	W	=	watts
25	ZDOL	=	poly(tetrafluoroethylene oxide-co-difluoromethylene oxide)α,ω diol

BACKGROUND

The availability of viable nanofabrication processes is a key factor to realizing the potential of nanotechnologies. In particular, the availability of viable nanofabrication processes is important to the fields of photonics, electronic, and proteomics. Traditional imprint lithographic (IL) techniques are an alternative to photolithography for manufacturing integrated circuits, micro- and nano-fluidic devices, and other devices with micron sized features. There

is a need in the art, however, for new materials to advance IL techniques. See Xia, Y., et al., *Angew. Chem. Int. Ed.*, **1998**, 37, 550-575; Xia, Y., et al., *Chem. Rev.*, **1999**, 99, 1823-1848; Resnick, D. J., et al., *Semiconductor International*, **2002**, June, 71-78; Choi, K. M., et al., *J. Am. Chem. Soc.*, **2003**, 125, 4060-4061; McClelland, G. M., et al., *Appl. Phys. Lett.*, **2002**, 81, 1483; Chou, S. Y., et al., *J. Vac. Sci. Technol. B*, **1996**, 14, 4129; Otto, M., et al., *Microelectron. Eng.*, **2001**, 57, 361; and Bailey, T., et al., *J. Vac. Sci. Technol., B*, **2000**, 18, 3571.

Imprint lithography comprises at least two areas: (1) so-called soft lithographic techniques, see Xia, Y., et al., *Angew. Chem. Int. Ed.*, **1998**, 37, 550-575, such as solvent-assisted micro-molding (SAMIM); micro-molding in capillaries (MIMIC); and microcontact printing (MCP); and (2) rigid imprint techniques, such as nano-contact molding (NCM), see McClelland, G. M., et al., *Appl. Phys. Lett.*, **2002**, 81, 1483; Otto, M., et al., *Microelectron. Eng.*, **2001**, 57, 361; "step and flash" imprint lithographic (S-FIL), see Bailey, T., et al., *J. Vac. Sci. Technol., B*, **2000**, 18, 3571; and nanoimprint lithography (NIL), see Chou, S. Y., et al., *J. Vac. Sci. Technol. B*, **1996**, 14, 4129.

Polydimethylsiloxane (PDMS) based networks have been the material of choice for much of the work in soft lithography. See Quake, S. R., et al., *Science*, **2000**, 290, 1536. The use of soft, elastomeric materials, such as PDMS, offers several advantages for lithographic techniques. For example, PDMS is highly transparent to ultraviolet (UV) radiation and has a very low Young's modulus (about 750 kPa), which gives it the flexibility required for conformal contact, even over surface irregularities without the potential for cracking. In contrast, cracking can occur with molds made from brittle, high-modulus materials, such as etched silicon and glass. See Bietsch, A., et al., *J. Appl. Phys.*, **2000**, 88, 4310-4318. Further, flexibility in molds facilitates easy release of the mold from masters and replicates without cracking and allows the mold to endure multiple imprinting steps without damaging fragile features.

Although PDMS offers some advantages in soft lithography applications, a number of properties inherent to PDMS severely limit its

capabilities in soft lithography. First, PDMS-based elastomers swell when exposed to most oil-soluble organic compounds. See Lee, J. N., et al., *Anal. Chem.*, 2003, 75, 6544-6554. Although this property is favorable in MCP applications because it allows the mold to adsorb organic inks, see Xia, Y., et al., *Angew. Chem. Int. Ed.*, 1998, 37, 550-575, resistance to swelling is critically important in nearly all other soft lithographic techniques, especially for SAMIM and MIMIC, and for IL techniques in which a mold is brought into contact with a small amount of curable organic monomer or resin. Otherwise, the fidelity of the features on the mold is lost and an unsolvable adhesion problem ensues due to infiltration of the curable liquid into the mold. Such problems commonly occur with PDMS-based molds because most organic liquids swell PDMS. Organic liquids, however, are the materials most desirable to mold.

Secondly, the surface energy of PDMS (~25 mN/m) is not low enough for soft lithography procedures that require high fidelity. For this reason, the patterned surface of PDMS-based molds is often fluorinated using a plasma treatment followed by vapor deposition of a fluoroalkyl trichlorosilane. See Xia, Y., et al., *Angew. Chem. Int. Ed.*, 1998, 37, 550-575.

Third, the most commonly-used commercially available form of the material used in PDMS molds, e.g., Sylgard 184® (Dow Corning Corporation, Midland, Michigan, United States of America) has a modulus that is too low (~1.5 MPa) for many applications. The low modulus of these commonly used PDMS materials results in sagging and bending of features and, as such, is not well suited for processes that require precise pattern placement and alignment. Although researchers have attempted to address this last problem, see Odom, T. W., et al., *J. Am. Chem. Soc.*, 2002, 124, 12112-12113; Odom, T. W. et al., *Langmuir*, 2002, 18, 5314-5320; Schmid, H., et al., *Macromolecules*, 2000, 33, 3042-3049; Csucs, G., et al., *Langmuir*, 2003, 19, 6104-6109; Trimbach, D., et al., *Langmuir*, 2003, 19, 10957-10961, the materials chosen still exhibit poor solvent resistance and require fluorination steps to allow for mold release.

Rigid materials, such as quartz glass and silicon, also have been used in imprint lithography. See Xia, Y., et al., *Angew. Chem. Int. Ed.*, 1998, 37,

550-575; Resnick, D. J., et al., *Semiconductor International*, **2002**, June, 71-78; McClelland, G. M., et al., *Appl. Phys. Lett.*, **2002**, 81, 1483; Chou, S. Y., et al., *J. Vac. Sci. Technol. B*, **1996**, 14, 4129; Otto, M., et al., *Microelectron. Eng.*, **2001**, 57, 361; and Bailey, T., et al., *J. Vac. Sci. Technol., B*, **2000**, 18, 3571; Chou, S. Y., et al., *Science*, **1996**, 272, 85-87; Von Werne, T. A., et al., *J. Am. Chem. Soc.*, **2003**, 125, 3831-3838; Resnick, D. J., et al., *J. Vac. Sci. Technol. B*, **2003**, 21, 2624-2631. Such materials are superior to PDMS in modulus and swelling resistance, but lack flexibility. Such lack of flexibility inhibits conformal contact with the substrate. Another drawback of rigid materials is the necessity to use a costly and difficult to fabricate hard mold, which is typically made by using conventional photolithography or e-beam lithography. See Chou, S. Y., et al., *J. Vac. Sci. Technol. B*, **1996**, 14, 4129. More recently, the need to repeatedly use expensive quartz glass or silicon molds in NCM processes has been eliminated by using an acrylate-based mold generated from casting a photopolymerizable monomer mixture against a silicon master. See McClelland, G. M., et al., *Appl. Phys. Lett.*, **2002**, 81, 1483, and Jung, G. Y., et al., *Nanoletters*, **2004**, ASAP.

Despite such advances, other disadvantages of fabricating molds from rigid materials include the necessity to use fluorination steps to the lower surface energy of the mold, see Resnick, D. J., et al., *Semiconductor International*, **2002**, June, 71-78, and the inherent problem of releasing a rigid mold from a rigid substrate without breaking or damaging the mold. See Resnick, D. J., et al., *Semiconductor International*, **2002**, June, 71-78; Bietsch, A., *J. Appl. Phys.*, **2000**, 88, 4310-4318. Khang, D. Y., et al., *Langmuir*, **2004**, 20, 2445-2448, have reported the use of rigid molds composed of thermoformed Teflon AF™ to address the surface energy problem. Fabrication of these molds, however, required high temperatures and pressures in a melt press, a process that could be damaging to the delicate features on a silicon wafer master. Further, these molds still exhibit the intrinsic drawbacks of other rigid materials outlined hereinabove. A clear and important problem of fabricating structures on semiconductor devices using molds or templates made from hard materials is the usual formation of

a "scum" layer that forms when a rigid template is brought into contact with a substrate. Even with elevated applied forces, it is very difficult to cleanly displace liquids during this process, which can result in the formation of a scum layer. Thus, there is a need in the art for a method of fabricating structures on a substrate, such as a semiconductor device, which does not result in the formation of a scum layer.

The fabrication of organic solvent resistant, microfluidic devices with features on the order of hundreds of microns from photocurable perfluoropolyether (PFPE) has been reported. See Rolland, J. P., et al., J. Am. Chem. Soc., 2004, 126, 2322-2323. PFPE-based materials are liquids at room temperature and can be photochemically cross-linked to yield tough, durable elastomers. Further, PFPE-based materials are highly fluorinated and resist swelling by organic solvents, such as methylene chloride and acetonitrile, which are desirable for use in microchemistry platforms based on elastomeric microfluidic devices. There is a need in the art, however, to apply PFPE-based materials to the fabrication of nanoscale devices.

Further, there is a need in the art for improved methods for forming a pattern on a substrate, such as method employing a patterned mask. See U. S. Patent No. 4,735,890 to Nakane et al.; U. S. Patent No. 5,147,763 to Kamitakahara et al.; U.S. Patent No. 5,259,926 to Kuwabara et al.; and International PCT Publication No. WO 99/54786 to Jackson et al., each of which is incorporated herein by reference in their entirety.

There is also a need in the art for an improved method for forming isolated structures that can be considered "engineered" structures, including but not limited to particles, shapes, and parts. Using traditional IL methods, the scum layer that almost always forms between structures acts to connect or link structures together, thereby making it difficult, if not impossible to harvest isolated structures.

There also is a need in the art for an improved method for forming micro- and nanoscale charged particles, in particle polymer electrets. The term "polymer electrets" refers to dielectrics with stored charge, either on the surface or in the bulk, and dielectrics with oriented dipoles, frozen-in or ferroelectric. On the macro scale, such materials are used, for example, for

electronic packaging and charge electret devices, such as microphones and the like. See Kressman, R., et al., *Space-Charge Electrets*, Vol. 2, Laplacian Press, 1999; and Harrison, J. S., et al., *Piezoelectric Polymers*, NASA/CR-2001-211422, ICASE Report No. 2001-43. Poly(vinylidene fluoride) (PVDF) is one example of a polymer electret material. In addition to PVDF, charge electret materials, such as PP, Teflon-FEP, and PTFE, also are considered polymer electrets.

Further, there is a need in the art for improved methods for delivering therapeutic agents, such as drugs, non-viral gene vectors, DNA, RNA, RNAi, and viral particles, to a target. See *Biomedical Polymers*, Shalaby, S. W., ed., Harner/Gardner Publications, Inc., Cincinnati, Ohio, 1994; *Polymeric Biomaterials*, Dumitriu, S., ed., Marcel Dekker, Inc., New York, New York, 1994; Park, K., et al., *Biodegradable Hydrogels for Drug Delivery*, Technomic Publishing Company, Inc., Lancaster, Pennsylvania, 1993; Gumargalieva, et al., *Biodegradation and Biodeterioration of Polymers: Kinetic Aspects*, Nova Science Publishers, Inc., Commack, New York, 1998; *Controlled Drug Delivery*, American Chemical Society Symposium Series 752, Park, K., and Mrsny, R. J., eds., Washington, D.C., 2000; *Cellular Drug Delivery: Principles and Practices*, Lu, D. R., and Oie, S., eds., Humana Press, Totowa, New Jersey, 2004; and *Bioreversible Carriers in Drug Design: Theory and Applications*, Roche, E. B., ed., Pergamon Press, New York, New York, 1987. For a description of representative therapeutic agents for use in such delivery methods, see U.S. Patent No. 6,159,443 to Hallahan, which is incorporated herein by reference in its entirety.

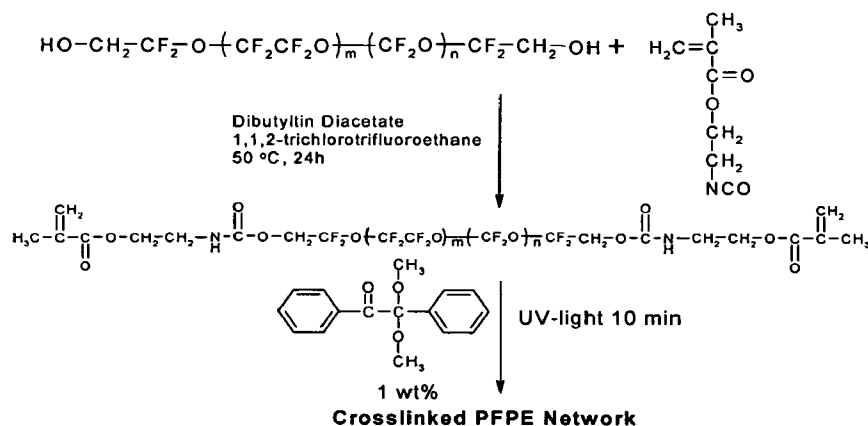
In sum, there exists a need in the art to identify new materials for use in imprint lithographic techniques. More particularly, there is a need in the art for methods for the fabrication of structures at the tens of micron level down to sub-100 nm feature sizes.

SUMMARY

The presently disclosed subject matter describes the use of fluorinated elastomer-based materials, in particular perfluoropolyether (PFPE)-based materials, in high-resolution soft or imprint lithographic applications, such as

micro- and nanoscale replica molding, and the first nano-contact molding of organic materials to generate high fidelity features using an elastomeric mold. Accordingly, the presently disclosed subject matter describes a method for producing free-standing, isolated nanostructures of any shape using soft or imprint lithography techniques.

A photocurable liquid PFPE exhibits ideal properties for soft lithography. A representative scheme for the synthesis and photocuring of functional perfluoropolyethers is provided in Scheme 1.



Scheme 1. Synthesis and Photocuring of Functional Perfluoropolyethers.

This PFPE material a low surface energy (about 12 mN/m), is non-toxic, UV transparent, highly gas permeable, and cures into a tough, durable, highly fluorinated elastomer with excellent release properties and resistance to swelling. The properties of these materials can be tuned over a wide range through the judicious choice of additives, fillers, reactive co-monomers, and functionalization agents. Such properties that are desirable to modify, include, but are not limited to, modulus, tear strength, surface energy, permeability, functionality, mode of cure, solubility and swelling characteristics, and the like. The non-swelling nature and easy release properties of the presently disclosed PFPE materials allows for nanostructures to be fabricated from any material. Further, the presently disclosed subject matter can be expanded to large scale rollers or conveyor

belt technology or rapid stamping that allow for the fabrication of nanostructures on an industrial scale.

5 The nanostructures described by the presently disclosed subject matter can be used in several applications, including, but not limited to, semiconductor manufacturing, especially used as molding etch barriers without scum layers for the fabrication of semiconductor devices; crystals; materials for displays; photovoltaics; optoelectronic devices; routers; gratings; radio frequency identification (RFID) devices; catalysts; fillers and additives; detoxifying agents; etch barriers; atomic force microscope (AFM) tips; parts
10 for nano-machines; the delivery of a therapeutic agent, such as a drug or genetic material; cosmetics; chemical mechanical planarization (CMP) particles; and porous particles and shapes of any kind that will enable the nanotechnology industry.

15 Certain objects of the presently disclosed subject matter having been stated hereinabove, which are addressed in whole or in part by the presently disclosed subject matter, other aspects and objects will become evident as the description proceeds when taken in connection with the accompanying Examples as best described herein below.

20 BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a schematic illustration of the presently disclosed method for forming freestanding nanostructures (jagged edges indicate a continuing structure).

25 Figure 2 is a schematic illustration of the presently disclosed method for fabricating isolated spherical nanoparticles.

Figure 3 is a schematic representation of the presently disclosed method for fabricating charged polymeric particles. (A) represents the electrostatic charging of the molded particle during polymerization or crystallization; (B) represents a charged nano-disc; (C) represents typical
30 random juxtapositioning of uncharged nano-discs; and (D) represents the spontaneous aggregation of charged nano-discs into chain-like structures.

Figure 4 is a schematic illustration of multilayer particles that can be formed using the presently disclosed soft lithography method.

Figure 5 is a schematic representation of a (A) the presently disclosed method for making three dimensional nanostructures using a soft lithography technique; and (B) an exemplary structure made by the presently disclosed soft lithography method.

5 Figure 6 is a schematic representation of imprint lithography processes resulting in a "scum layer."

Figure 7 is a schematic representation of the presently disclosed imprint lithography method, which eliminates the "scum layer" by using a functionalized, non-wetting substrate and a non-wetting stamp.

10

DETAILED DESCRIPTION

The presently disclosed subject matter will now be described more fully hereinafter with reference to the accompanying Examples, in which representative embodiments are shown. The presently disclosed subject matter can, however, be embodied in different forms and should not be construed as limited to the embodiments set forth herein. Rather, these
15 embodiments are provided so that this disclosure will be thorough and complete, and will fully convey the scope of the embodiments to those skilled in the art.

20 Unless otherwise defined, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this presently described subject matter belongs. All publications, patent applications, patents, and other references mentioned herein are incorporated by reference in their entirety.

25 Throughout the specification and claims, a given chemical formula or name shall encompass all optical and stereoisomers, as well as racemic mixtures where such isomers and mixtures exist.

1. Formation of Isolated Nanostructures

30 In some embodiments, the presently disclosed subject matter provides a method for making isolated nanostructures. Turning now to Figure 1, in some embodiments, the process comprises an etched substrate, such as a silicon wafer, which is etched in the desired pattern to form a patterned

master. See Figure 1A. A liquid fluoropolymer composition, such as a PFPE-based precursor, is then poured onto the etched substrate and cured, for example through exposure to UV light, thereby curing it in the desired pattern. See Figure 1B. The cured PFPE is then removed from the etched substrate.
5 to form a patterned stamp. See Figure 1C.

Separately, a substrate, such as a silicon wafer, is treated or is coated with a non-wetting material. See Figure 1D. In some embodiments, the non-wetting material comprises a PFPE elastomer that can be further exposed to UV light and cured to form a thin, non-wetting layer on the surface of the
10 substrate. In some embodiments, the substrate is made non-wetting to the liquid by treating the substrate with a small molecule, such as an alkyl- or fluoroalkyl-silane. A droplet of curable resin, monomer, or solution in which the desired nanostructures will be formed is then placed on the coated wafer. See Figure 1D. The patterned stamp formed in Step 1C is then brought into
15 contact with the droplet so that it takes the desired pattern. See Figure 1E. Without being bound to any particular theory, once pressure is applied, the affinity of the PFPE stamp for the non-wetting coating or surface treatment on the substrate in combination with the non-wetting behavior of the PFPE-based template material and surface treated or coated substrate causes the
20 liquid to be excluded from all areas except for those inside the pattern. See Figure 1F.

Further, in embodiments essentially free of non-wetting or low wetting materials with which to sandwich the small drop of the curable resin, monomer, or solution, a "scum" layer that interconnects the objects being
25 stamped forms. The resin/monomer can then be photocured through the stamp or thermally cured while under pressure.

In some embodiments, a material, including but not limited to a polymer, an organic compound, or an inorganic compound, can be dissolved in a solvent, patterned, and the solvent can be released. See Figure 1F.

30 Once the material is patterned, the entire stamp is removed from the coated substrate. See Figure 1G. The cured nanostructures are confined to the patterned areas of the stamp. See Figure 1G. The structures could be

retained on the substrate in defined regions once the stamp is removed. This embodiment would be desirable for use in the manufacture of semiconductor devices where essentially scum-layer free features could be used as etch barriers or as conductive, semiconductive, or dielectric layers directly, mitigating or reducing the need to use traditional and expensive photolithographic processes. In addition, the structures can be removed from the substrate or from the stamp by a variety of methods which include but are not limited to: (1) reapplying the stamp to a surface that has an affinity for the nanostructures; (2) deforming the stamps, or using other mechanical methods, including sonication, in such a manner that the structures are naturally released from the stamp; (3) swelling the stamp reversibly with supercritical carbon dioxide or another solvent that will extrude the structures; and (4) washing the stamp with a solvent that has an affinity for the nanostructures and will wash them out of the patterned stamp. See Figure 1H.

More particularly, in some embodiments, a method for preparing a patterned structure is disclosed, the method comprising:

- (a) disposing a volume of liquid material between two surface elements, wherein at least one of the two surface elements comprises a patterned area;
- (b) contacting the two surface elements by applying contact pressure to create a point of contact between the two surface elements and confine the liquid material to the patterned area of at least one surface element;
- (c) forming a structure within the patterned area from the liquid material of at least one surface element; and
- (d) removing at least one of the surface elements to provide a structure.

In some embodiments, the patterned area comprises a nanoscale patterned area. In some embodiments, the structure comprises a nanoscale structure.

In some embodiments, at least one of the surface elements comprises an elastomeric material. In some embodiments, at least one of the surface elements comprises a patterned polymeric stamp. In some embodiments, the patterned polymeric stamp is prepared by a method comprising:

- 5 (a) providing a patterned substrate;
- (b) contacting the patterned substrate with a polymer precursor;
- (c) curing the polymer precursor to form a patterned polymeric stamp comprising patterned areas; and
- 10 (d) removing the patterned polymeric stamp from the patterned substrate.

In some embodiments, the patterned substrate comprises an etched substrate. In some embodiments, the etched substrate comprises an etched silicon wafer. In some embodiments, the patterned substrate comprises a nanoscale patterned substrate.

15 In some embodiments, the polymer precursor comprises a fluoropolymer precursor. In some embodiments, the fluoropolymer precursor comprises a liquid perfluoropolyether precursor. In some embodiments, the curing of the polymer precursor is performed by exposing the polymer precursor to actinic radiation. In some embodiments, the actinic radiation is
20 selected from one of thermal and electromagnetic radiation. In some embodiments, the actinic radiation comprises electromagnetic radiation. In some embodiments, the electromagnetic radiation comprises ultraviolet radiation.

 In some embodiments, the patterned polymeric stamp comprises a
25 gas-permeable or solvent permeable polymer. In some embodiments, the patterned polymeric stamp comprises a crosslinked, fluorinated polymer. In some embodiments, the crosslinked, fluorinated polymer comprises a crosslinked perfluoropolyether-derived polymer. In some embodiments, other reactive co-monomers or modifiers were used or added to modify the
30 properties of the polymeric stamp. In some embodiments, the patterned polymeric stamp comprises an optically transparent polymer.

In some embodiments, the patterned area of the at least one of the surface elements comprises structural features. In some embodiments, the

structural features range from about 10 microns to about 1 nanometer in size. In some embodiments, the structural features range from about 10 microns to about 1 micron in size. In some embodiments, the structural features range from about 1 micron to about 100 nm in size. In some embodiments, the structural features range from about 100 nm to about 1 nm in size. In some embodiments, the structural features comprise a channel.

In some embodiments, the liquid material is selected from one of a curable material and a solution. In some embodiments, the curable material is selected from one of a curable resin and a curable monomer. In some embodiments, the method further comprises curing the curable material while the material is confined to the patterned area (e.g., a nanoscale patterned area) of at least one of the surface elements.

In some embodiments, the solution comprises a solvent and a soluble material selected from the group consisting of a polymer, an organic compound, and an inorganic compound. In some embodiments, the solvent is removed while the soluble material is confined within the patterned area (e.g., a nanoscale patterned area) of at least one of the surface elements.

In some embodiments, at least one of the surface elements comprises a microelectronic device. In some embodiments, the microelectronic device comprises a silicon wafer.

In some embodiments, at least one of the surface elements is coated or treated with a non-wetting or low-wetting material. In some embodiments, the non-wetting or low-wetting material comprises a perfluoropolyether precursor. In some embodiments, the perfluoropolyether precursor is cured to form a thin layer of perfluoropolyether elastomer on at least one of the surface elements. In some embodiments, the curing of the perfluoropolyether precursor is performed by one of exposing the perfluoropolyether precursor to ultraviolet radiation and thermally curing the perfluoropolyether precursor. In some embodiments, the non-wetting or low-wetting treatment comprises a silane.

In some embodiments, the structure comprises a nanostructure. In some embodiments, the nanostructure comprises a free standing nanostructure.

2. Formation of Spherical Particles Through "Liquid Reduction"

In some embodiments, the presently disclosed subject matter provides a "liquid reduction" process for forming spherical particles. Without being bound to any particular theory, the non-wetting nature of the presently disclosed PFPE materials allows for the generation of spherical particles. This process is illustrated in Figure 2. The patterned stamp is placed on top of a drop of curable liquid, which is in contact with a substrate. The liquid then enters the channels of the patterned stamp, but a "scum layer" remains between the stamp and substrate. A pressure is applied to the stamp, thereby forming a contact point between the stamp and the substrate and eliminating the scum layer. A higher pressure is then applied to the stamp, thereby forming smaller liquid particles inside the channels and forcing more liquid out of the channels. The original contact pressure is then applied. The gas permeable nature of the stamp allows for part of the void to be filled with nitrogen or another gas, thereby leaving a spherical droplet. Once this liquid reduction is achieved, the particles are cured in their spherical shape and removed from the stamp.

More particularly, in some embodiments, the method comprises:

- (a) reducing the volume of the liquid material confined in the stamp by one of:
 - (i) applying additional contact pressure to at least one of the surface elements to reduce the volume of the liquid material formed within the patterned area of at least one of the surface elements and extrude additional liquid material from the patterned area; and
 - (ii) allowing some of the liquid or solvent of a multicomponent system to evaporate or permeate through the stamp;
- (b) reducing the additional contact pressure from the surface element;
- (c) introducing gas within the patterned area of at least one of the surface elements;

- (d) forming at least one or more structures within the patterned area of at least one of the surface elements; and
- (e) releasing the structure or structures from the patterned area of at least one of the surface elements.

5 In some embodiments, the structures are particles, for example spherical particles. In some embodiments, the particles comprise monodisperse particles. In some embodiments, the particles are nanoscale particles, and the nanoscale particles can comprise a spherical shape. In some embodiments, the nanoscale particles can comprise monodisperse
10 nanoscale particles. In some embodiments, the method further comprises applying an electric field during the forming of the particles to provide a charged polymeric particle.

 In some embodiments, the presently disclosed subject matter describes a method for stamping out polymeric nano- to micro-electrets by
15 applying an electric field during the polymerization and/or crystallization step during molding (**A** in Figure 3) to yield a charged polymeric particle (**B** in Figure 3). In some embodiments, the charged polymeric particles spontaneously aggregate into chain-like structures (**D** in Figure 3) instead of the random configurations shown in **C** of Figure 3.

20 In some embodiments, the charged polymeric particle comprises a polymeric electret. In some embodiments, the polymeric electret comprises a polymeric nano-electret. In some embodiments, the charged polymeric particles aggregate into chain-like structures. In some embodiments, the charged polymeric particles comprise an additive for an electro-rheological
25 device. In some embodiments, the electro-rheological device is selected from the group consisting of clutches and active dampening devices. In some embodiments, the charged polymeric particles comprise nano-piezoelectric devices. In some embodiments, the nano-piezoelectric devices are selected from the group consisting of actuators, switches, and mechanical sensors.

30

3. Formation of Multilayer Structures

In some embodiments, the presently disclosed subject matter provides a process for forming multilayer structures, including multilayer particles. In some embodiments, the multilayer structures, including multilayer particles, comprise nanoscale multilayer structures. In some embodiments, multilayer structures are formed by depositing multiple thin layers of immiscible liquids and/or solutions onto a substrate and forming particles as described by any of the methods hereinabove. The immiscibility of the liquid can be based on any physical characteristic, including but not limited to density, polarity, and volatility. Examples of possible morphologies of the presently disclosed subject matter are illustrated in Figure 4 and include, but are not limited to, multi-phase sandwich structures, core-shell particles, and internal emulsions, microemulsions and/or nano-sized emulsions.

More particularly, in some embodiments, the method comprises disposing a plurality of immiscible liquids between the two surface elements to form a multilayer structure, e.g., a multilayer nanostructure. In some embodiments, the multilayer structure comprises a multilayer particle. In some embodiments, the multilayer structure comprises a structure selected from the group consisting of multi-phase sandwich structures, core-shell particles, internal emulsions, microemulsions, and nanosized emulsions.

4. Fabrication of Complex Multidimensional Structures

In some embodiments, the currently disclosed subject matter provides a process for fabricating complex, multidimensional structures. In some embodiments, complex multidimensional structures can be formed by performing the process illustrated in Figure 1. In some embodiments, the process comprises imprinting onto a patterned substrate that is aligned with the patterned stamp (instead of imprinting onto a smooth substrate) to generate isolated multidimensional structures that are cured and released as described hereinabove. An illustration of the process for forming complex multidimensional structures and examples of such structures is provided in Figure 5.

More particularly, in some embodiments, both surface elements comprise a patterned area. In some embodiments, the method further comprises aligning the patterned area of the surface elements before applying contact pressure to at least one of the surface elements to form a patterned structure. In some embodiments, the patterned structure comprises a nanoscale patterned structure. In some embodiments, the patterned structure comprises a multidimensional structure. In some embodiments, the multidimensional structure comprises a nanoscale multidimensional structure. In some embodiments, the multidimensional structure comprises a plurality of structural features. In some embodiments, the structural features comprise a plurality of heights. In some embodiments, a microelectronic device produced by the method is described herein. With this technique any structures imaginable, including "dual damscene" structures for microelectronics can be generated. In some embodiments, the microelectronic device is selected from the group consisting of integrated circuits, semiconductor particles, quantum dots, and dual damascene structures. In some embodiments, the microelectronic device exhibits certain physical properties selected from the group consisting of etch resistance, low dielectric constant, high dielectric constant, conducting, semiconducting, insulating, porosity, and non-porosity.

5. Imprint Lithography Free of a Residual "Scum Layer"

A characteristic of imprint lithography that has restrained its full potential is the formation of a "scum layer" once the resin is patterned. The "scum layer" comprises residual resin that remains between the stamp and the substrate. See Figure 6. In some embodiments, the presently disclosed subject matter provides a process for using imprint lithography to generate patterns essentially free of a scum layer. See Figure 7. The substrate is functionalized with a non-wetting material. The non-wetting material further comprises functional groups that bind to the curable resin. The non-wetting material includes, but is not limited to, a mixture of trichloro or trialkoxy silanes, or a single trichloro or trialkoxy silane comprising non-wetting and

reactive functional groups. Without being bound to any particular theory, the non-wetting nature of both the stamp and the substrate will drive the resin out except in patterned areas. Upon curing, the functional groups of the substrate react with the resin and bind it to the substrate. The substrate can be etched with traditional lithographic techniques.

More particularly, in some embodiments, at least one of the surface elements comprises a functionalized surface element. In some embodiments, the functionalized surface element is functionalized with a non-wetting material. In some embodiments, the non-wetting material comprises functional groups that bind to the liquid material. In some embodiments, the non-wetting material is selected from the group consisting of a trichloro silane, a trialkoxy silane, a trichloro silane comprising non-wetting and reactive functional groups, a trialkoxy silane comprising non-wetting and reactive functional groups, and mixtures thereof.

In some embodiments, the point of contact between the two surface elements is free of liquid material. In some embodiments, the point of contact between the two surface elements comprises residual liquid material. In some embodiments, the height of the residual liquid material is less than 30% of the height of the structure. In some embodiments, the height of the residual liquid material is less than 20% of the height of the structure. In some embodiments, the height of the residual liquid material is less than 10% of the height of the structure. In some embodiments, the height of the residual liquid material is less than 5% of the height of the structure. In some embodiments, the volume of liquid material is less than the volume of a patterned area. In some embodiments, substantially all of the volume of liquid material is confined to a patterned area of at least one of the surface elements. In some embodiments, having the point of contact between the two surface elements free of liquid material retards slippage between the two surface elements.

6. Removing the Patterned Structure from the Surface Element

In some embodiments, the removing of the patterned structure (e.g., a patterned nanostructure) from at least one of the surface elements is performed by one of:

- 5 (a) reapplying the surface element containing the patterned structure to a surface that has an affinity for the patterned structure;
- (b) deforming the surface element containing the patterned structure such that the patterned structure is released from the surface element;
- 10 (c) swelling the surface element containing the patterned structure with a first solvent to extrude the patterned structure; and
- (d) washing the surface element containing the patterned structure with a second solvent that has an affinity for the patterned structure.
- 15

In some embodiments, the first solvent comprises supercritical fluid carbon dioxide. In some embodiments, the first solvent comprises water. In some embodiments, the first solvent comprises an aqueous solution comprising water and a detergent. In embodiments, the deforming the surface element is performed by applying a mechanical force to the surface element. In some embodiments, the method of removing the patterned structure further comprises a sonication method.

20

7. Methods of Forming a Pattern on a Substrate or a Surface

25 In some embodiments, the method of forming a pattern on a substrate comprises:

- (a) providing a template, wherein the template comprises a first surface and a plurality of recesses extending from the first surface toward an opposing second surface and a plurality of non-recessed areas, wherein the plurality of recesses and non-recessed areas defines a plurality of structural features in the first surface of the template;
- 30

- (b) positioning the template and the substrate in a spaced relationship to each other so that a gap is created between the template and the substrate;
- (c) disposing a volume of curable liquid in the gap between the template and the substrate;
- (d) contacting the template with the volume of curable liquid;
- (e) curing the curable liquid; and
- (f) removing the template from the cured curable liquid to provide a pattern on a substrate.

In some embodiments, the template comprises an elastomeric material. In some embodiments, the template consists of an elastomeric material. In some embodiments, the template is an elastomeric material. In some embodiments, the elastomeric material comprises a crosslinked, fluorinated polymer. In some embodiments, the crosslinked, fluorinated polymer comprises a crosslinked, perfluoropolyether derivative. In some embodiments, the template comprises a template prepared by a soft lithography or by an imprint lithography technique.

In some embodiments, the volume of curable liquid fills the gap between the template and the substrate. In some embodiments, the volume of liquid fills the plurality of recesses of the template. In some embodiments, the template and the substrate comprise non-wetting materials with respect to the curable liquid material. In some embodiments, the contacting the template with the volume of curable liquid further comprises contacting the non-recessed areas of the template with the substrate, thereby eliminating all of the volume of curable liquid between the non-recessed areas of the template and the substrate. In some embodiments, essentially no scum layer is formed.

In some embodiments, a method of making a microelectronic device by employing the patterned substrate is disclosed. In some embodiments, the microelectronic device comprises a semiconductor.

In some embodiments, a method of making a particle by employing the patterned substrate is disclosed. In some embodiments, the particle further comprises a therapeutic agent. In some embodiments, the therapeutic agent

comprises a drug. In some embodiments, the therapeutic agent comprises genetic material. In some embodiments, the genetic material is selected from the group consisting of a non-viral gene vector, DNA, RNA, RNAi, and a viral particle.

5 In some embodiments, a method of making a display device by employing the patterned substrate is disclosed. In some embodiments, the display device comprises an Organic Light Emitting Diode. In some embodiments, the Organic Light Emitting Diode comprises a patterning Organic Light Emitting Diode.

10 In some embodiments, a method of forming a pattern on a surface is disclosed, the method comprising selectively exposing the surface of an article to an agent by:

- 15 (a) shielding a first portion of the surface of the article with a masking system, wherein the masking system comprises a elastomeric mask in conformal contact with the surface of the article; and
- 20 (b) applying an agent to be patterned within the masking system to a second portion of the surface of the article, while preventing application of the agent to the first portion shielded by the masking system.

25 In some embodiments, the elastomeric mask comprises a plurality of channels. In some embodiments, each of the channels has a cross-sectional dimension of less than about 1 millimeter. In some embodiments, each of the channels has a cross-sectional dimension of less than about 1 micron. In some embodiments, each of the channels has a cross-sectional dimension of less than about 100 nm. In some embodiments, each of the channels has a cross-sectional dimension of about 1 nm. In some embodiments, the agent swells the elastomeric mask less than 25%.

30 In some embodiments, the agent comprises an organic electroluminescent material or a precursor thereof. In some embodiments, the method further comprising allowing the organic electroluminescent material to form from the agent at the second portion of the surface, and

establishing electrical communication between the organic electroluminescent material and an electrical circuit.

5 In some embodiments, the agent comprises a liquid or is carried in a liquid. In some embodiments, the agent comprises the product of chemical vapor deposition. In some embodiments, the agent comprises a product of deposition from a gas phase. In some embodiments, the agent comprises a product of e-beam deposition, evaporation, or sputtering. In some
10 embodiments, the agent comprises a product of electrochemical deposition. In some embodiments, the agent comprises a product of electroless deposition. In some embodiments, the agent is applied from a fluid precursor. In some embodiments, comprises a solution or suspension of an inorganic compound. In some embodiments, the inorganic compound hardens on the second portion of the article surface.

15 In some embodiments, the fluid precursor comprises a suspension of particles in a fluid carrier. In some embodiments, the method further comprises allowing the fluid carrier to dissipate thereby depositing the particles at the first region of the article surface. In some embodiments, the fluid precursor comprises a chemically active agent in a fluid carrier. In some
20 embodiments, the method further comprises allowing the fluid carrier to dissipate thereby depositing the chemically active agent at the first region of the article surface.

In some embodiments, the chemically active agent comprises a polymer precursor. In some embodiments, the method further comprises forming a polymeric article from the polymer precursor. In some
25 embodiments, the chemically active agent comprises an agent capable of promoting deposition of a material. In some embodiments, the chemically active agent comprises an etchant. In some embodiments, the method further comprises allowing the second portion of the surface of the article to be etched. In some embodiments, the method further comprises removing
30 the elastomeric mask of the masking system from the first portion of the article surface while leaving the agent adhered to the second portion of the article surface.

8. Method of Delivering a Therapeutic Agent

In some embodiments, a method of delivering a therapeutic agent to a target is disclosed, the method comprising:

- (a) providing a particle produced by a method comprising:
 - (i) disposing a volume of liquid material between two surface elements, wherein at least one of the two surface elements comprises a patterned area;
 - (ii) contacting the two surface elements by applying contact pressure to create a point of contact between the two surface elements and confine the liquid material to the patterned area of at least one surface element;
 - (iii) forming at least one or more particles within the patterned area of at least one of the surface elements; and
 - (iv) releasing the particles from the patterned area of at least one of the surface elements.
- (b) admixing the therapeutic agent with the particle; and
- (c) delivering the particle comprising the therapeutic agent to the target.

In some embodiments, the particle has a diameter of less than 100 microns. In some embodiments, the particle has a diameter of less than 10 microns. In some embodiments, the particle has a diameter of less than 1 micron. In some embodiments, the particle has a diameter of less than 100 nm. In some embodiments, the particle has a diameter of less than 10 nm. In some embodiments, the therapeutic agent is selected from one of a drug and genetic material, such as a non-viral gene vector, DNA, RNA, RNAi, and a viral particle. In some embodiments, the particle comprises a biodegradable polymer. In some embodiments, the biodegradable polymer is selected from the group consisting of a polyester, a polyanhydride, a polyamide, a phosphorous-based polymer, a poly(cyanoacrylate), a polyurethane, a polyorthoester, a polydihydropyran, and a polyacetal. In some embodiments, the polyester is selected from the group consisting of polylactic acid, polyglycolic acid, poly(hydroxybutyrate), poly(ϵ -caprolactone), poly(β -malic acid), and poly(dioxanones). In some embodiments, the

polyanhydride is selected from the group consisting of poly(sebacic acid), poly(adipic acid), and poly(terphthalic acid). In some embodiments, the polyamide is selected from the group consisting of poly(imino carbonates) and polyaminoacids. In some embodiments, the phosphorous-based polymer is selected from the group consisting of polyphosphates, polyphosphonates, and polyphosphazenes. In some embodiments, the polymer is responsive to stimuli, such as pH, light or temperature. Responses to such stimuli can include swelling, which can facilitate release of its cargo, or degradation.

10 Examples

The following Examples have been included to provide guidance to one of ordinary skill in the art for practicing representative embodiments of the presently disclosed subject matter. In light of the present disclosure and the general level of skill in the art, those of skill can appreciate that the following Examples are intended to be exemplary only and that numerous changes, modifications, and alterations can be employed without departing from the scope of the presently disclosed subject matter.

1. Representative Procedure for Synthesis and Curing Photocurable Perfluoropolyethers

In some embodiments, the synthesis and curing of PFPE materials of the presently disclosed subject matter is performed by using the method described by Rolland, J. P., et al., *J. Am. Chem. Soc.*, **2004**, *126*, 2322-2323. Briefly, this method involves the methacrylate-functionalization of a commercially available PFPE diol ($M_n = 3800$ g/mol) with isocyanatoethyl methacrylate. Subsequent photocuring of the material is accomplished through blending with 1 wt% of 2,2-dimethoxy-2-phenylacetophenone and exposure to UV radiation ($\lambda = 365$ nm).

More particularly, in a typical preparation of perfluoropolyether dimethacrylate (PFPE DMA), poly(tetrafluoroethylene oxide-co-difluoromethylene oxide) α,ω diol (ZDOL, average M_n ca. 3,800 g/mol, 95%, Aldrich Chemical Company, Milwaukee, Wisconsin, United States of America) (5.7227g, 1.5 mmol) was added to a dry 50 mL round bottom flask and

purged with argon for 15 minutes. 2-isocyanatoethyl methacrylate (EIM, 99%, Aldrich) (0.43 mL, 3.0 mmol) was then added via syringe along with 1,1,2-trichlorotrifluoroethane (Freon 113 99%, Aldrich) (2 mL), and dibutyltin diacetate (DBTDA, 99%, Aldrich) (50 μ L). The solution was immersed in an oil bath and allowed to stir at 50 °C for 24 h. The solution was then passed through a chromatographic column (alumina, Freon 113, 2 x 5 cm). Evaporation of the solvent yielded a clear, colorless, viscous oil, which was further purified by passage through a 0.22- μ m polyethersulfone filter.

In a representative curing procedure for PFPE DMA, 1 wt% of 2,2-dimethoxy-2-phenyl acetophenone (DMPA, 99% Aldrich), (0.05g, 2.0 mmol) was added to PFPE DMA (5g, 1.2 mmol) along with 2 mL Freon 113 until a clear solution was formed. After removal of the solvent, the cloudy viscous oil was passed through a 0.22- μ m polyethersulfone filter to remove any DMPA that did not disperse into the PFPE DMA. The filtered PFPE DMA was then irradiated with a UV source (Electro-Lite Corporation, Danbury, Connecticut, United States of America, UV curing chamber model no. 81432-ELC-500, λ = 365 nm) while under a nitrogen purge for 10 min. This resulted in a clear, slightly yellow, rubbery material.

2. Representative Fabrication of a PFPE DMA Device

In some embodiments, a PFPE DMA device, such as a stamp, was fabricated according to the method described by Rolland, J. P., et al., J. Am. Chem. Soc., 2004, 126, 2322-2323. Briefly, the PFPE DMA containing a photoinitiator, such as DMPA, was spin coated (800 rpm) to a thickness of 20 μ m onto a Si wafer containing the desired photoresist pattern. This coated wafer was then placed into the UV curing chamber and irradiated for 6 seconds. Separately, a thick layer (about 5 mm) of the material was produced by pouring the PFPE DMA containing photoinitiator into a mold surrounding the Si wafer containing the desired photoresist pattern. This wafer was irradiated with UV light for one minute. Following this, the thick layer was removed. The thick layer was then placed on top of the thin layer such that the patterns in the two layers were precisely aligned, and then the

entire device was irradiated for 10 minutes. Once complete, the entire device was peeled from the Si wafer with both layers adhered together.

5 It will be understood that various details of the presently disclosed subject matter can be changed without departing from the scope of the presently disclosed subject matter. Furthermore, the foregoing description is for the purpose of illustration only, and not for the purpose of limitation.

CLAIMS

What is claimed is:

1. A method for preparing a patterned structure, the method comprising:
 - 5 (a) disposing a volume of liquid material between two surface elements, wherein at least one of the two surface elements comprises a patterned area;
 - (b) contacting the two surface elements by applying contact pressure to create a point of contact between the two surface
10 elements and confine the liquid material to the patterned area of at least one surface element;
 - (c) forming a structure within the patterned area from the liquid material of at least one surface element; and
 - (d) removing at least one of the surface elements to provide a
15 structure.
2. The method of Claim 1, wherein at least one of the surface elements comprises an elastomeric material.
3. The method of Claim 1, wherein the patterned area comprises a nanoscale patterned area.
- 20 4. The method of Claim 1, wherein at least one of the surface elements comprises a patterned polymeric stamp.
5. The method of Claim 4, wherein the patterned polymeric stamp is prepared by the method comprising:
 - 25 (a) providing a patterned substrate;
 - (b) contacting the patterned substrate with a polymer precursor;
 - (c) curing the polymer precursor to form a patterned polymeric stamp comprising patterned areas; and
 - (d) removing the patterned polymeric stamp from the patterned substrate.
- 30 6. The method of Claim 5, wherein the patterned substrate comprises a nanoscale patterned substrate.
7. The method of Claim 5, wherein the patterned substrate comprises an etched substrate.

8. The method of Claim 7, wherein the etched substrate comprises an etched silicon wafer.
9. The method of Claim 5, wherein the polymer precursor comprises a fluoropolymer precursor.
- 5 10. The method of Claim 9, wherein the fluoropolymer precursor comprises a liquid perfluoropolyether precursor.
11. The method of Claim 5, wherein the curing of the polymer precursor is performed by exposing the polymer precursor to actinic radiation.
- 10 12. The method of Claim 11, wherein the actinic radiation is selected from one of thermal and electromagnetic radiation.
13. The method of Claim 12, wherein the actinic radiation comprises electromagnetic radiation.
14. The method of Claim 13, wherein the electromagnetic radiation comprises ultraviolet radiation.
- 15 15. The method of Claim 5, wherein the patterned polymeric stamp comprises a gas-permeable polymer.
16. The method of Claim 5, wherein the patterned polymeric stamp comprises a solvent-permeable polymer.
17. The method of Claim 5, wherein the patterned polymeric stamp
20 comprises a crosslinked, fluorinated polymer.
18. The method of Claim 17, wherein the crosslinked, fluorinated polymer comprises a crosslinked perfluoropolyether polymer.
19. The method of Claim 17, wherein the crosslinked, fluorinated polymer comprises a modified crosslinked, fluorinated polymer.
- 25 20. The method of Claim 19, wherein a co-monomer or modifier is employed to modify the crosslinked, fluorinated polymer.
21. The method of Claim 5, wherein the patterned polymeric stamp comprises an optically transparent polymer.
22. The method of Claim 1, wherein the patterned area of the at least one
30 of the surface elements comprise structural features.
23. The method of Claim 22, wherein the structural features range from about 10 microns to about 1 nanometer in size.

24. The method of Claim 23, wherein the structural features range from about 10 microns to about 1 micron in size.
25. The method of Claim 23, wherein the structural features range from about 1 micron to about 100 nm in size.
- 5 26. The method of Claim 23, wherein the structural features range from about 100 nm to about 1 nm in size.
27. The method of Claim 22, wherein the structural features comprise a channel.
- 10 28. The method of Claim 1, wherein the liquid material is selected from one of a curable material and a solution.
29. The method of Claim 28, wherein the curable material is selected from one of a curable resin and a curable monomer.
- 15 30. The method of Claim 29, further comprising curing the curable material while the material is confined to the patterned area of at least one of the surface elements.
31. The method of Claim 28, wherein the solution comprises a solvent and a soluble material, wherein the soluble material is selected from the group consisting of a polymer, an organic compound, and an inorganic compound.
- 20 32. The method of Claim 31, wherein the solvent is removed while the soluble material is confined within the patterned area of at least one of the surface elements.
33. The method of Claim 1, wherein at least one of the surface elements comprises a microelectronic device.
- 25 34. The method of Claim 33, wherein the microelectronic device comprises a silicon wafer.
35. The method of Claim 1, wherein at least one of the surface elements is treated or coated with a non-wetting or low-wetting material.
- 30 36. The method of Claim 35, wherein the non-wetting or low-wetting material comprises a perfluoropolyether precursor.
37. The method of Claim 36, wherein the perfluoropolyether precursor is cured to form a thin layer of perfluoropolyether elastomer on at least one of the surface elements.

38. The method of Claim 37, wherein the curing of the perfluoropolyether precursor is performed by one of exposing the perfluoropolyether precursor to ultraviolet radiation and thermally curing the perfluoropolyether precursor.
- 5 39. The method of Claim 35, wherein the non-wetting or low-wetting material is selected from one of an alkylsilane and a fluoroalkylsilane.
40. A structure produced by the method of Claim 1.
41. The method of Claim 1, wherein the structure comprises a nanostructure.
- 10 42. A nanostructure produced by the method of Claim 41.
43. The method of Claim 1, wherein the structure comprises a free standing structure.
44. A freestanding structure produced by the method of Claim 43.
45. The method of Claim 43, wherein the free standing structure comprises a nanostructure.
- 15 46. The method of Claim 1, further comprising disposing a plurality of immiscible liquids between the two surface elements.
47. The method of Claim 1, wherein the structure further comprises a multilayer structure.
- 20 48. The method of Claim 47, wherein the multilayer structure comprises a nanoscale multilayer structure.
49. The method of Claim 47, wherein the multilayer structure comprises a multilayer particle.
50. The method of Claim 49, wherein the multilayer particle comprises a nanoscale multilayer particle.
- 25 51. The method of Claim 47, wherein the multilayer structure comprises a structure selected from the group consisting of multi-phase sandwich structures, core-shell particles, internal emulsions, microemulsions, and nanosized emulsions.
- 30 52. A multilayer structure produced by the method of Claim 47.
53. A multilayer particle produced by the method of Claim 49.
54. The method of Claim 1, further comprising:

- 5
- (a) reducing the volume of the liquid material confined to at least one of the surface elements by one of:
- (i) applying additional contact pressure to at least one of the surface elements to reduce the volume of the liquid material formed within the patterned area of at least one of the surface elements and extrude additional liquid material from the patterned area; and
- (ii) allowing some of the liquid to evaporate or permeate through the surface element;
- 10
- (b) reducing the additional contact pressure from the surface element;
- (c) introducing gas within the patterned area of at least one of the surface elements;
- 15
- (d) forming at least one or more structures within the patterned area of at least one of the surface elements; and
- (e) releasing the structure or structures from the patterned area of at least one of the surface elements.
55. The method of Claim 54, wherein the structures comprise particles.
56. The method of Claim 55, wherein the particles comprise a spherical shape.
- 20
57. The method of Claim 55, wherein the particles comprise monodisperse particles.
58. The method of Claim 55, wherein the particles comprise nanoscale particles.
- 25
59. The method of Claim 54, further comprising applying an electric field during the forming of the structure or structures within the patterned area of at least one of the surface elements to form charged polymeric particles.
- 30
60. The method of Claim 59, wherein the charged polymeric particles comprise polymeric electrets.
61. The method of Claim 60, wherein the polymeric electrets comprise polymeric nano-electrets.

62. The method of Claim 59, wherein the charged polymeric particles aggregate into chain-like structures.
63. The method of Claim 59, wherein the charged polymeric particles comprise an additive for an electro-rheological device.
- 5 64. The method of Claim 63, wherein the electro-rheological device is selected from the group consisting of clutches and active dampening devices.
65. The method of Claim 59, wherein the charged polymeric particles comprise nano-piezoelectric devices.
- 10 66. The method of Claim 65, wherein the nano-piezoelectric devices are selected from the group consisting of actuators, switches, and mechanical sensors.
67. A particle produced by the method of Claim 54.
68. Monodisperse particles produced by the method of Claim 54.
- 15 69. A charged polymeric particle produced by the method of Claim 59.
70. A polymeric electret produced by the method of Claim 60.
71. A polymeric nano-electret produced by the method of Claim 61.
72. A nano-piezoelectric device produced by the method of Claim 65.
73. The method of Claim 1, wherein both surface elements comprise a patterned area.
- 20 74. The method of Claim 73, further comprising aligning the patterned areas of the surface elements before applying contact pressure to at least one of the surface elements to form a patterned structure.
75. The method of Claim 74, wherein the patterned structure comprises a multidimensional structure.
- 25 76. The method of Claim 75, wherein the multidimensional structure comprises a plurality of structural features.
77. The method of Claim 76, wherein the structural features comprise a plurality of heights.
- 30 78. The method of Claim 73, wherein the patterned area comprises a patterned nanoscale area.
79. The method of Claim 74, wherein the patterned structure comprises a patterned nanoscale structure.

80. The method of Claim 75, wherein the multidimensional structure comprises a multidimensional nanoscale structure.
81. A microelectronic device produced by the method of Claim 74.
- 5 82. The method of Claim 81, wherein the microelectronic device is selected from the group consisting of integrated circuits, semiconductor particles, quantum dots, and dual damascene structures.
- 10 83. The method of Claim 81, wherein the microelectronic device exhibits a physical property selected from the group consisting of etch resistance, low dielectric constant, high dielectric constant, conducting, semiconducting, insulating, porosity, non-porosity, and combinations thereof.
- 15 84. The method of Claim 1, wherein at least one of the surface elements comprises a functionalized surface element.
85. The method of Claim 84, wherein the functionalized surface element is functionalized with a non-wetting material.
86. The method of Claim 85, wherein the non-wetting material comprises functional groups that bind to the liquid material.
- 20 87. The method of Claim 86, wherein the non-wetting material is selected from the group consisting of a trichloro silane, a trialkoxy silane, a trichloro silane comprising non-wetting and reactive functional groups, a trialkoxy silane comprising non-wetting and reactive functional groups, and mixtures thereof.
- 25 88. The method of Claim 1, wherein the point of contact between the two surface elements is free of liquid material.
89. The method of Claim 1, wherein the point of contact between the two surface elements comprises residual liquid material.
90. The method of Claim 89, wherein the residual liquid material has a height less than 30% of the height of the structure.
- 30 91. The method of Claim 89, wherein the residual liquid material has a height less than 20% of the height of the structure.
92. The method of Claim 89, wherein the residual liquid material has a height less than 10% of the height of the structure.

93. The method of Claim 89, wherein the residual liquid material has a height less than 5% of the height of the structure.
94. The method of Claim 1, wherein the volume of liquid material is less than the volume of the patterned area.
- 5 95. The method of Claim 94, wherein substantially all of the volume of liquid material is confined to the patterned area of at least one of the surface elements.
96. The method of Claim 95, wherein having the point of contact between the two surface elements free of liquid material retards slippage between the two surface elements.
- 10 97. The method of Claim 1, wherein the removing of the patterned structure from at least one of the surface elements is performed by one of:
- 15 (a) reapplying the surface element containing the structure to a second surface element that has an affinity for the patterned structure;
- (b) deforming the surface element containing the structure such that the structure is released from the surface element;
- (c) swelling the surface element containing the structure with a first solvent to extrude the structure; and
- 20 (d) washing the surface element containing the structure with a second solvent that has an affinity for the structure.
98. The method of Claim 97, wherein the first solvent is selected from the group consisting of supercritical fluid carbon dioxide, water, and an aqueous solution comprising water and a detergent.
- 25 99. The method of Claim 97, wherein the deforming the surface element is performed by applying a mechanical force to the surface element.
100. The method of Claim 97, further comprising a sonication method.
101. A method of forming a pattern on a substrate, the method comprising:
- 30 (a) providing a template, wherein the template comprises a first surface and a plurality of recesses extending from the first surface toward an opposing second surface and a plurality of non-recessed areas, wherein the plurality of recesses and non-

- recessed areas defines a plurality of structural features in the first surface of the template;
- 5 (b) positioning the template and the substrate in a spaced relationship to each other so that a gap is created between the template and the substrate;
- (c) disposing a volume of curable liquid in the gap between the template and the substrate;
- (d) contacting the template with the volume of curable liquid;
- (e) curing the curable liquid; and
- 10 (f) removing the template from the cured curable liquid to provide a pattern on a substrate.
102. The method of Claim 101, wherein the template is an elastomeric material.
103. The method of Claim 101, wherein the template comprises an elastomeric material.
- 15 104. The method of Claim 102 or 103, wherein the elastomeric material comprises a crosslinked, fluorinated polymer.
105. The method of Claim 104, wherein the crosslinked, fluorinated polymer comprises a crosslinked, perfluoropolyether derivative.
- 20 106. The method of Claim 101, wherein the template comprises a template prepared by one of a soft lithography technique and an imprint lithography technique.
107. The method of Claim 101, wherein the volume of curable liquid fills the gap between the template and the substrate.
- 25 108. The method of Claim 101, wherein the volume of liquid fills the plurality of recesses of the template.
109. The method of Claim 101, wherein the template and the substrate comprise non-wetting materials with respect to the curable liquid material.
- 30 110. The method of Claim 101, wherein the contacting the template with the volume of curable liquid further comprises contacting the non-recessed areas of the template with the substrate, thereby eliminating all of the

- volume of curable liquid between the non-recessed areas of the template and the substrate.
111. The method of Claim 110, wherein essentially no scum layer is formed.
112. A patterned substrate produced by the method of Claim 101.
- 5 113. A method of making a microelectronic device by employing the patterned substrate of Claim 101.
114. The method of Claim 113, wherein the microelectronic device comprises a semiconductor.
115. A method of making a particle by employing the patterned substrate of
10 Claim 112.
116. The method of Claim 115, wherein the particle further comprises a therapeutic agent.
117. The method of Claim 116, wherein the therapeutic agent is selected from one of a drug and genetic material.
- 15 118. The method of Claim 117, wherein the therapeutic agent comprises a drug.
119. The method of Claim 117, wherein the genetic material is selected from the group consisting of a non-viral gene vector, DNA, RNA, RNAi, and a viral particle.
- 20 120. The method of Claim 119, wherein the therapeutic agent comprises a non-viral gene vector.
121. The method of Claim 119, wherein the therapeutic agent comprises a viral particle.
122. A method of making a display device by employing the patterned
25 substrate of Claim 112.
123. The method of Claim 122, wherein the display device comprises an Organic Light Emitting Diode.
124. The method of Claim 123, wherein the Organic Light Emitting Diode comprises a patterning Organic Light Emitting Diode.
- 30 125. A method of forming a pattern on a surface, the method comprising selectively exposing the surface of an article to an agent by:
- (a) shielding a first portion of the surface of the article with a masking system, wherein the masking system comprises a

elastomeric mask in conformal contact with the surface of the article; and

- (b) applying an agent to be patterned within the masking system to a second portion of the surface of the article, while preventing application of the agent to the first portion shielded by the masking system.

126. The method of Claim 125, wherein the elastomeric mask comprises a plurality of channels.

127. The method of Claim 126, wherein each of the channels has a cross-sectional dimension of less than about 1 millimeter.

128. The method of Claim 126, wherein each of the channels has a cross-sectional dimension of less than about 1 micron.

129. The method of Claim 126, wherein each of the channels has a cross-sectional dimension of less than about 100 nm.

130. The method of Claim 126, wherein each of the channels has a cross-sectional dimension of about 1 nm.

131. The method of Claim 125, wherein the agent swells the elastomeric mask less than 25%.

132. The method of Claim 125, wherein the agent comprises an organic electroluminescent material or a precursor thereof.

133. The method of Claim 132, further comprising:

(a) allowing the organic electroluminescent material to form from the agent at the second portion of the surface, and

(b) establishing electrical communication between the organic electroluminescent material and an electrical circuit.

134. The method of Claim 125, wherein the agent comprises a liquid or is carried in a liquid.

135. The method of Claim 125, wherein the agent comprises the product of chemical vapor deposition.

136. The method of Claim 125, wherein the agent comprises a product of deposition from a gas phase.

137. The method of Claim 125, wherein the agent comprises a product of e-beam deposition, evaporation, or sputtering.

138. The method of Claim 125, wherein the agent comprises a product of electrochemical deposition.
139. The method of Claim 125, wherein the agent comprises a product of electroless deposition.
- 5 140. The method of Claim 125, wherein the agent is applied from a fluid precursor.
141. The method of Claim 140, wherein the fluid precursor comprises a solution or suspension of an inorganic compound.
- 10 142. The method of Claim 141, wherein the inorganic compound hardens on the second portion of the article surface.
143. The method of Claim 140, wherein the fluid precursor comprises a suspension of particles in a fluid carrier.
144. The method of Claim 143, further comprising allowing the fluid carrier to dissipate thereby depositing the particles at the first region of the article surface.
- 15 145. The method of Claim 140, wherein the fluid precursor comprises a chemically active agent in a fluid carrier.
146. The method of Claim 145, further comprising allowing the fluid carrier to dissipate thereby depositing the chemically active agent at the first region of the article surface.
- 20 147. The method of Claim 145, wherein the chemically active agent comprises a polymer precursor.
148. The method of Claim 147, further comprising forming a polymeric article from the polymer precursor.
- 25 149. The method of Claim 145, wherein the chemically active agent comprises an agent capable of promoting deposition of a material.
150. The method of Claim 145, wherein the chemically active agent comprises an etchant.
- 30 151. The method of Claim 150, further comprising allowing the second portion of the surface of the article to be etched.
152. The method of Claim 125, further comprising removing the elastomeric mask of the masking system from the first portion of the article surface

while leaving the agent adhered to the second portion of the article surface.

153. A method of delivering a therapeutic agent to a target, the method comprising:

- 5 (a) providing a particle produced by a method comprising
- (i) disposing a volume of liquid material between two surface elements, wherein at least one of the two surface elements comprises a patterned area;
- 10 (ii) contacting the two surface elements by applying contact pressure to create a point of contact between the two surface elements and confine the liquid material to the patterned area of at least one surface element;
- (iii) forming at least one or more particles within the patterned area of at least one of the surface elements; and
- 15 (iv) releasing the particles from the patterned area of at least one of the surface elements.
- (b) admixing the therapeutic agent with the particle; and
- (c) delivering the particle comprising the therapeutic agent to the target.

20 154. The method of Claim 153, wherein the therapeutic agent is selected from one of a drug and genetic material.

155. The method of Claim 154, wherein the therapeutic agent comprises a drug.

25 156. The method of Claim 154, wherein the genetic material is selected from the group consisting of a non-viral gene vector, DNA, RNA, RNAi, and a viral particle.

157. The method of Claim 153, wherein the particle comprises a biodegradable polymer.

30 158. The method of Claim 157, wherein the biodegradable polymer is selected from the group consisting of a polyester, a polyanhydride, a polyamide, a phosphorous-based polymer, a poly(cyanoacrylate), a polyurethane, a polyorthoester, a polydihydropyran, and a polyacetal.

159. The method of Claim 158, wherein the polyester is selected from the group consisting of polylactic acid, polyglycolic acid, poly(hydroxybutyrate), poly(ϵ -caprolactone), poly(β -malic acid), and poly(dioxanones).
- 5 160. The method of Claim 158, wherein the polyanhydride is selected from the group consisting of poly(sebacic acid), poly(adipic acid), and poly(terphthalic acid).
161. The method of Claim 158, wherein the polyamide is selected from the group consisting of poly(imino carbonates) and polyaminoacids.
- 10 162. The method of Claim 158, wherein the phosphorous-based polymer is selected from the group consisting of polyphosphates, polyphosphonates, and polyphosphazenes.
163. The method of Claim 157, wherein the biodegradable polymer further comprises a polymer that is responsive to a stimulus.
- 15 164. The method of Claim 163, wherein the stimulus is selected from the group consisting of pH, light, and temperature.
165. The method of Claim 153, wherein the particle has a diameter less than 100 microns.
166. The method of Claim 153, wherein the particle has a diameter less than 10 microns.
- 20 167. The method of Claim 153, wherein the particle has a diameter less than 1 micron.
168. The method of Claim 153, wherein the particle has a diameter less than 100 nm.
- 25 169. The method of Claim 153, wherein the particle has a diameter less than 10 nm.

ABSTRACT OF THE DISCLOSURE

The presently disclosed subject matter describes the use of fluorinated elastomer-based materials, in particular perfluoropolyether (PFPE)-based materials, in high-resolution soft or imprint lithographic applications, such as micro- and nanoscale replica molding, and the first nano-contact molding of organic materials to generate high fidelity features using an elastomeric mold. Accordingly, the presently disclosed subject matter describes a method for producing free-standing, isolated nanostructures of any shape using soft or imprint lithography techniques.

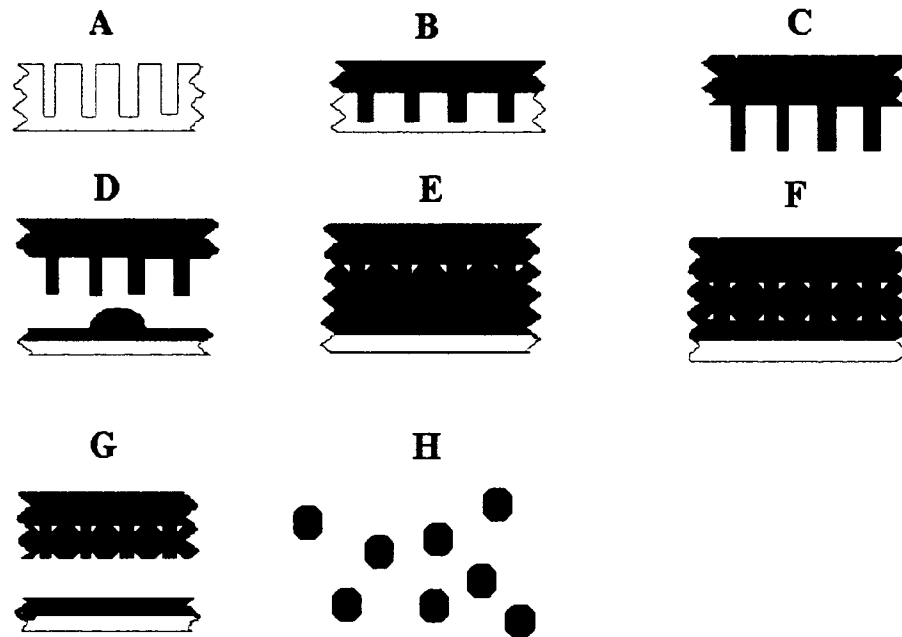


Fig. 1

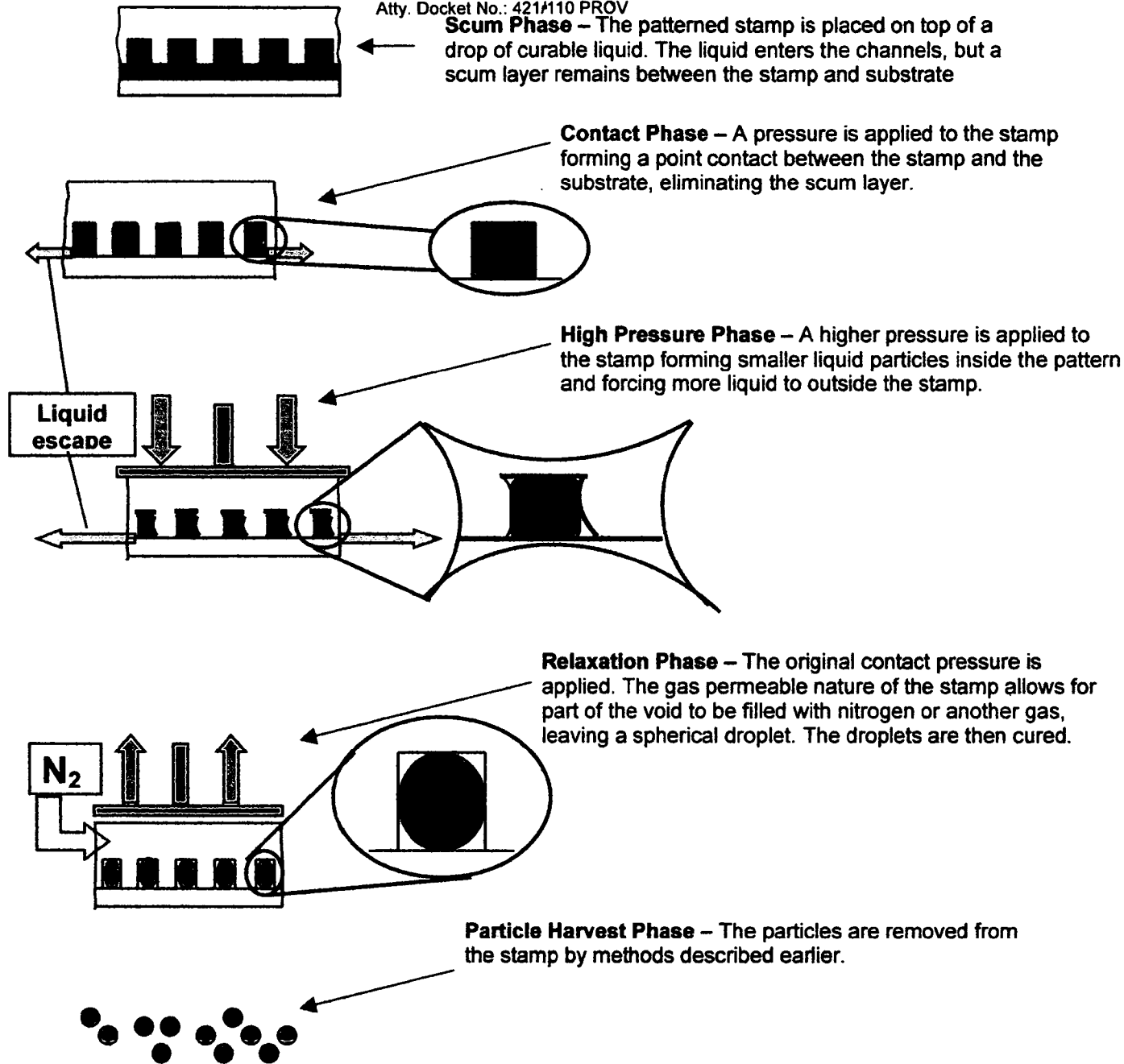


Fig. 2

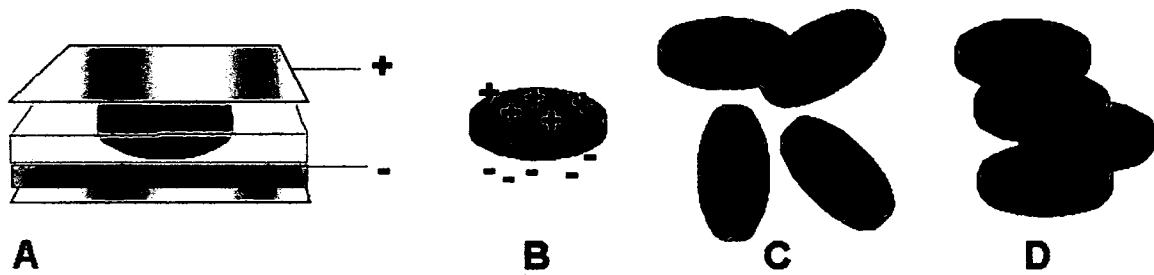


Fig. 3

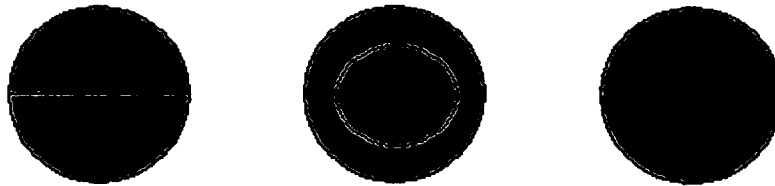


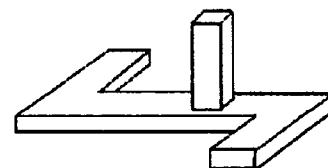
Fig. 4

Deposit and Align



A

**Press, Cure and
Release**



B

Fig. 5

Title: METHODS FOR FABRICATING
ISOLATED MICRO-AND NANO-
STRUCTURES USING SOFT OR
IMPRINT LITHOGRAPHY

Applicant(s): DeSimone et al.

Atty. Docket No.: 421/110 PROV

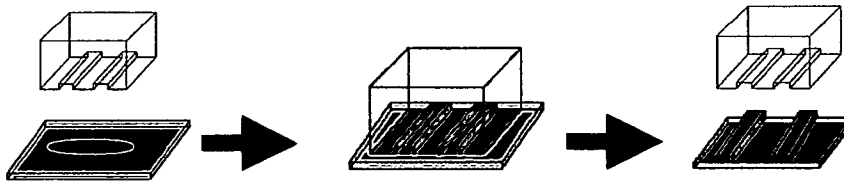


Fig. 6

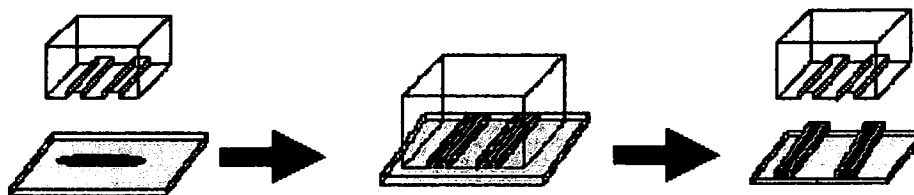


Fig. 7